

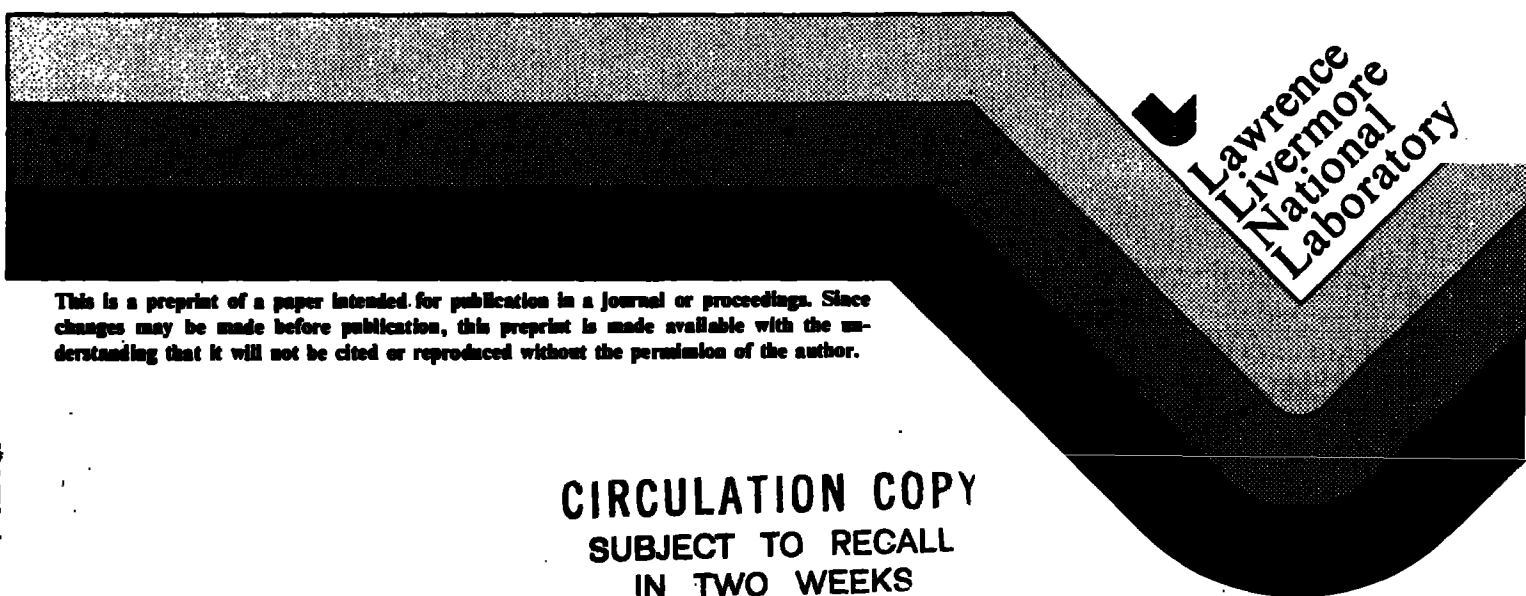
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Theoretical Methods for the Study of Transition  
Metals in Crystals

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# Theoretical Methods for the Study of Transition Metals in Crystals

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## I. Introduction

The characterization of the electronic structure of impurities in solids impacts a large class of phenomena and devices. It is particularly important for the systematic development of new solid state laser media. The large number of ion-host combinations that must be studied in order to optimize the linear and non-linear optical properties and the thermal and mechanical properties of the laser precludes a case by case experimental investigation. This suggests that an aggressive theoretical effort to determine the optical properties of these materials will be useful in the search for new tunable solid state lasers.

Unlike the Bloch states of a perfect crystal, the electronic states associated with impurities are localized on a very few atoms. Because their energy levels are usually well separated from those of the host crystal, the electronic spectroscopy of transition metal and rare earth ion impurities offers a wealth of information. The theoretical methods used to describe the properties of transition metals in crystals do not differ in principle from those used to treat atoms and molecules. The ion impurity and the neighboring crystal atoms define a molecular cluster that can be studied with a variety of empirical, semi-empirical, and ab initio methods. These include crystal field theory, semi-empirical molecular orbital theory, X-alpha and ab initio methods. The purpose of our study is to accurately locate the position of excited electronic states, calculate transition probabilities for absorption and emission, and determine the potential energy surfaces for lattice vibrations. This information will allow us to determine equilibrium geometries, vibrational frequencies and the probabilities for intersystem crossing and radiationless decay. At present this requires an ab initio treatment, although other approaches may be useful if they can be shown to be sufficiently accurate.

The state of our ability to predict and analyze the optical spectra of impurity metals in crystals with ab initio methods is behind similar studies on molecules. Although ab initio molecular orbital methods were applied to this problem over 20 years ago by SUGANO and SHULMAN[1], current calculations continue to give large errors in the predicted energy level splittings. In the earlier calculations, limitations on the accuracy were imposed by small basis sets and the neglect of electron correlation. This was due to the size and speed of available computers and codes. In addition to the quality of the basis sets, other factors that need to be considered are the effects of the crystal lattice beyond the nearest neighbors, relativistic corrections, and spin-orbit

interaction. We are currently including these factors in our theoretical calculations on transition metals in various crystal environments. Large basis set open shell Hartree-Fock (HF) calculations are being carried out on atom clusters to simulate the important effects of the crystal field and covalent bonding. A new configuration interaction code is being developed that will include the effects of both electron correlation and spin-orbit coupling[2]. The other important relativistic contributions are introduced by using an effective core potential derived from Dirac-Fock calculations on the free ion to replace the core electrons of the metal[3,4,5].

Recent experimental studies by McCLURE and co-workers[6] on  $\text{Cu}^+$  in alkali halide crystals have provided a wealth of quantitative information to which we can compare our theoretical results. In the following sections calculations on  $\text{Cu}^+:\text{NaF}$  and  $\text{Cu}^+:\text{NaCl}$  clusters are discussed and compared to experiment and to recent X-alpha calculations.

## II. Details of the Cluster Calculations

The cubic cluster for  $\text{Cu}^+$  in NaF is shown in Fig. 1. The  $\text{Cu}^+$  impurity is located at the center, the  $\text{F}^-$  ions are on the faces and at the corners of the cube, and the  $\text{Na}^+$  ions are on the edges and on the axes outside the cube. All electrons on the  $\text{Cu}^+$  ion were included in the calculations. The inner shell 1s electrons on the six nearest neighbor  $\text{F}^-$  ions were replaced by an effective core potential[7] and the eight  $\text{F}^-$  ions at the corners of the cube were approximated by point charges. The ten electrons on the  $\text{Na}^+$  ions were also replaced by an effective core potential[8]. An external lattice potential was not included in this calculation, therefore the cluster has a net positive charge. This and the point charge approximation for the second shell of fluoride ions are not necessary, but do not compromise the accuracy of the present calculations.

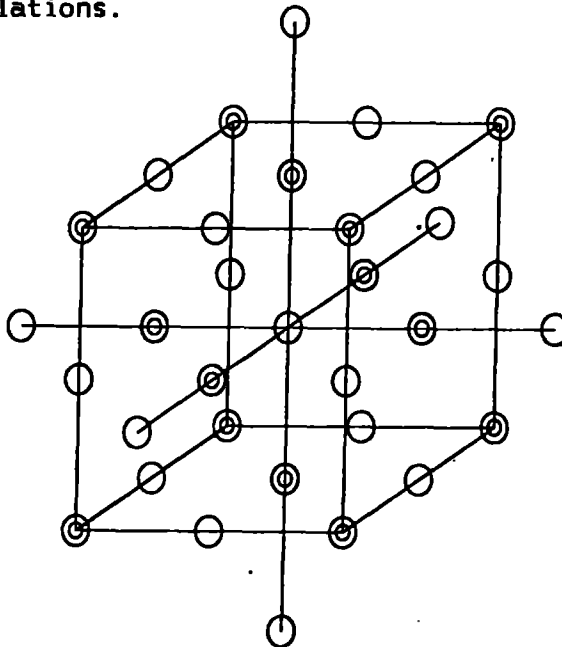


Fig. 1. The  $\text{Cu}^+:\text{NaF}$  cluster.

The gaussian basis set for the fluoride ion is from KAHN et al.[7] augmented with a diffuse 2p function as recommended by DUNNING and HAY[9]. Comparison of the  $F^-$  basis set with and without this extra 2p function illustrates the important effects that even a small difference in the basis set can make. As shown in Table I, the calculated electron affinity of fluorine is greatly improved by the addition of the single diffuse function. Note however the best HF value in Table I is still far from the experimental value of 3.4[eV] [10]. BORCH and DUNNING[11] have shown how the theoretical electron affinity can be systematically improved beyond the HF value until good agreement with experiment is achieved. Seriously underestimating the value of the electron affinity leads to an inaccurate charge distribution for the cluster and as a result the metal impurity will not experience the correct crystal field.

Table I. Basis set effects on the energies of F and  $F^-$

Basis set	[2s2p]		[2s2p] + 2p(0.074)	
Atom	F	$F^-$	F	$F^-$
$E_{HF}(a.u.)$	-23.9984	-24.0142	-23.9995	-23.0443
$\epsilon_{2s}$	-1.5682	-1.0055	-1.5736	-1.0708
$\epsilon_{2p}$	-0.7003	-0.1143	-0.7047	-0.1731
EA		-0.432 eV		-1.22 eV

An example of this is given in Table II. The doubly positive vanadium ion was surrounded by six fluoride ions in an octahedral coordination. The VF distance was fixed at 3.78[a.u.] close to the experimental value for  $V^{+2}$  in fluoride crystals. Table II gives the electron populations on the atoms in the cluster for the two  $F^-$  basis sets from a HF calculation on the  $^4A_{2g}$  ground state.

Table II. Fluorine basis set effects on the atomic populations of the  $VF_6^{+4}$  cluster

Basis Set	Atom	s	p	d	Total
[2s2p]	V	6.16	12.38	3.70	22.24
	F	11.58	35.18	0.	46.76
[2s3p]	V	6.08	12.04	3.19	21.31
	F	11.61	36.08	0.	47.69

VF distance = 3.78[a.u.]

The smaller basis set predicts that more than one electronic charge is transferred to the  $V^{+2}$  ion from the six  $F^-$  ions. By improving the electron affinity with the extra 2p function the population on vanadium correctly corresponds to the electronic configuration  $1s^2 2s^2 3s^2 2p^6 3p^6 3d^3$  of the ground state with only a reasonable amount of charge transfer.

The gaussian basis set for the  $Cu^+$  ion was taken from WACHTERS[12]. Here again the accuracy of the calculation can be greatly improved by adding a single function and efficiently contracting the primitive gaussian basis set. HAY[13] has determined the exponent of a single gaussian 3d function to be added to the WACHTERS basis set and HOOD et al.[14] have shown how to flexibly contract the primitive basis set in addition to augmenting it with additional p and d functions. Table III illustrates the effects of varying the  $Cu^+$  basis set. Hartree-Fock calculations with two variations of WACHTERS' basis set were carried out on the ground state of neutral Cu and for the ground and excited states of  $Cu^+$ . The contraction for basis set I was taken from WACHTERS[12] and for basis set II from HOOD et al.[14]. The primitive sets are identical except that basis set II was augmented with an additional 3d function as suggested by HAY[13]. The results for each basis set are compared to the numerical HF calculations of FISCHER[15] and to experiment[16]. It is clear that the single additional 3d function has a dramatic effect on the excitation energies for  $Cu^+$ . Both basis sets are in reasonable agreement with the HF value for the ionization potential of Cu, however basis I overestimates the  $3d^{10} \rightarrow 3d^9 4s$  excitation energy of  $Cu^+$  by nearly an electron volt. Basis set II is in good agreement with the numerical HF value. Of course, due to the neglect of electron correlation differences in the ground and excited states of  $Cu^+$ , the HF excitation energies are in error by  $\sim 1.5$  [eV].

Table III. Basis set effects on the energy levels of  $Cu^+$

State	Basis I	Basis II	Numerical HF	Experiment
$3d^{10} 4s^2 S$	-1638.8025 a.u.	-1638.9033	-1638.9505	-
$3d^{10} 1S$	6.23 eV	6.43 eV	6.41 eV	7.72 eV
$3d^9 4s^3 D$	8.63	7.76	7.69	10.53
$3d^9 4s^1 D$	9.16	8.19	-	10.97

Basis I (14s11p5d)/[8s6p2d] {62111111,511211,32}

Basis II (14s11p6d)/[10s9p3d] {5111111111,311111111,411}

### III. Results for the $\text{Cu}^+:\text{NaF}$ Cluster

Using basis set II for  $\text{Cu}^+$  and the  $[2s3p]$  basis for  $\text{F}^-$ , the HF energies for the lowest five states were calculated for the cluster shown in Fig. 1. These are the  $^1A_{1g}$  state which has a  $3d^{10}$   $\text{Cu}^+$  configuration and the  $^1,^3E_g$  and  $^1,^3T_{2g}$  states which have a  $3d^9 4s$   $\text{Cu}^+$  configuration. For these preliminary calculations, no basis functions were centered on the  $\text{Na}^+$  ions. The effective core potentials describe the 10 core electrons of  $\text{Na}^+$  and in addition to contributing to the crystal field for the  $\text{Cu}^+$  ion, they provide the correct repulsive interaction with the electrons on the  $\text{F}^-$  ions. This is important for the determination of the equilibrium positions of the ions. By fixing all of the ions except the six nearest neighbor  $\text{F}^-$  ions at the NaF distance of 4.379[a.u.], the potential curves for the  $a_{1g}$  symmetric stretch motion of these ions were determined as shown in Fig. 2.

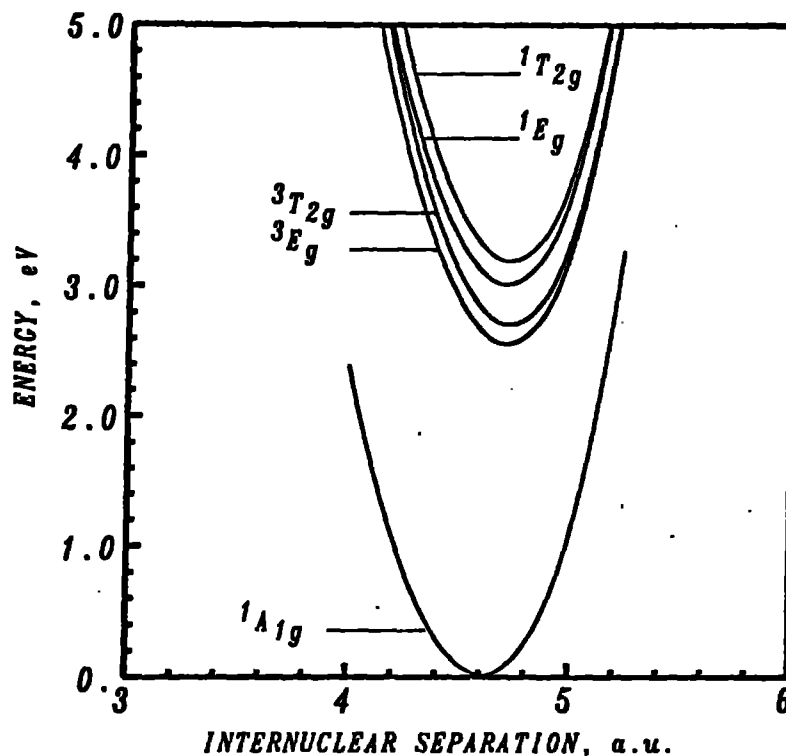


Fig. 2. Symmetric stretch potential energy curves for  $\text{Cu}^+:\text{NaF}$ .

The curves show that the equilibrium CuF distance for the ground state is 4.62[a.u.] which is somewhat longer than for NaF. The excited state distances are 4.71[a.u.] for the  $^3E_g$  and  $^1E_g$  states and 4.72[a.u.] for the  $^3T_{2g}$  and  $^1T_{2g}$  states.

The vertical excitation energies are compared to the positions of the absorption bands measured by PAYNE et al.[17] in Table IV.

Table IV. Comparison of excitation energies for  $\text{Cu}^+:\text{NaF}$  to experiment

State	Re(A)	$\Delta E(\text{cm}^{-1})$ calculated	$\Delta E(\text{cm}^{-1})$ experiment <sup>a</sup>
$^1\text{A}_{1g}$	2.44	0.	
$^3\text{E}_g$	2.49	21224	31200
$^3\text{T}_{2g}$	2.50	22593	32600
$^1\text{E}_g$	2.49	24852	32200, 34600 <sup>b</sup> , 33500 <sup>c</sup>
$^1\text{T}_{2g}$	2.50	26507	36400

a) Reference[17]

b) Jahn-Teller components from ref.[17].

c). Band peak, from average of Jahn-Teller components.

As was the case for  $\text{Cu}^+$ , the  $\text{Cu}^+:\text{NaF}$  calculations do not account for the electron correlation differences between the ground and excited states. Consequently the excited states are each about  $10000[\text{cm}^{-1}]$  too low (the average of the Jahn-Teller components of the  $^1\text{E}_g$  state is only  $8648[\text{cm}^{-1}]$  too low). The HF calculations on the excited states of the free  $\text{Cu}^+$  gave correlation errors of  $\sim 12000[\text{cm}^{-1}]$ . While placing the  $\text{Cu}^+$  ion in the NaF host reduces the correlation error, both theory and experiment show that the excitation energies are increased by more than  $1.0[\text{eV}]$ . The nearly constant difference between theory and experiment shown in Table IV is encouraging, since a uniform shift in the calculated levels will bring them into excellent agreement with the measured band peaks. This confirms the accuracy of the basis sets and the cluster approximation used here and suggests that when configuration interaction is included in future calculations total agreement with experiment will be obtained.

#### IV. Results for the $\text{Cu}^+:\text{NaCl}$ Cluster

By simply replacing the fluorine effective core potentials with those of HAY et al.[18] for chlorine and using the chlorine basis set suggested by KAHN[19] augmented with a diffuse p function with an exponent of 0.049 as determined by DUNNING and HAY[9], similar calculations have been carried out for  $\text{Cu}^+:\text{NaCl}$ . The symmetric stretch potential energy curves are shown in Fig. 3 which give the equilibrium  $\text{CuCl}$  distances for each state as  $^1\text{A}_{1g}$ , 5.11[a.u.],  $^1,^3\text{E}$ , 5.33[a.u.],  $^3\text{T}_{2g}$ , 5.34[a.u.], and  $^1\text{T}_{2g}$ , 5.35[a.u.]. The ground state distance is shorter than the normal NaCl spacing of 5.31[a.u.] in contrast to  $\text{Cu}^+:\text{NaF}$  where the nearest  $\text{F}^-$  ions moved away from the  $\text{Cu}^+$  ion. The HF excitation energies are compared to the X-alpha calculations of CHERMETTE and PEDRINI[20] and the spectra of PAYNE et al.[21] in Table V.



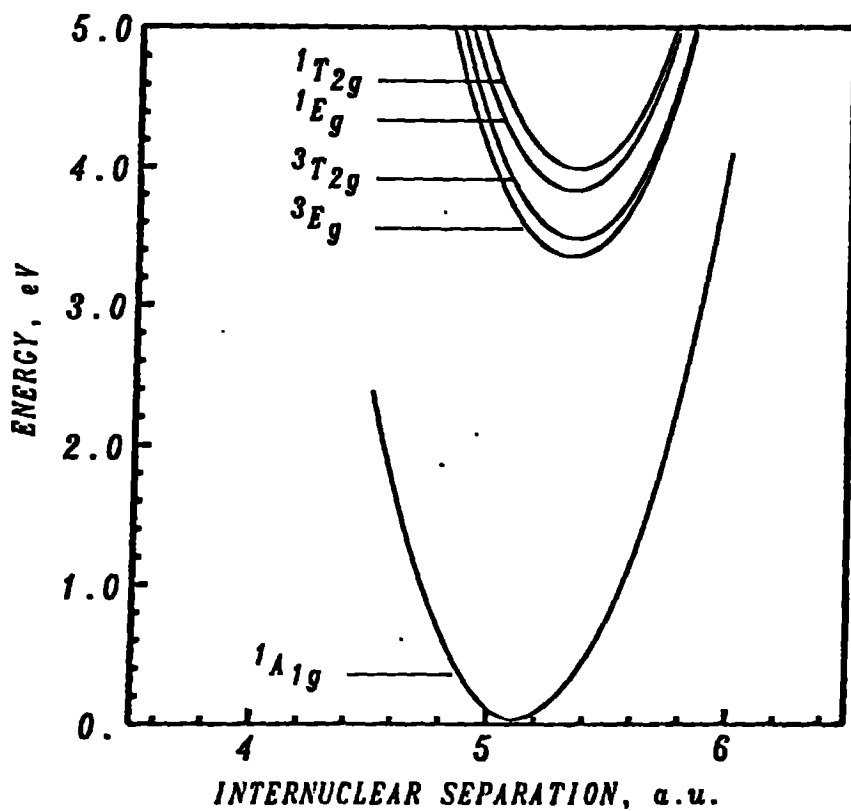


Fig. 3. The symmetric stretch potential energy curves for  $\text{Cu}^+:\text{NaCl}$

Table V. Comparison of Hartree-Fock, X-alpha, and experimental excitation energies for  $\text{Cu}^+:\text{NaCl}$ <sup>a</sup>

State	HF	X-alpha <sup>b</sup>	Experiment <sup>c</sup>
$3E_g$	3.59	3.61	
$3T_{2g}$	3.77	4.13	
$1E_g$	4.08	3.87	4.36, 4.51 <sup>d</sup>
$1T_{2g}$	4.29	4.448	4.77

a) All units are in electron volts.

b) Reference[20]

c) Reference[21]

d) Estimated band peak from the average of the Jahn-Teller components.

The X-alpha excitation energies are for the calculated equilibrium ground state distance of 5.79[a.u.] while the HF values are for the CuCl distance of 5.11[a.u.] found from Fig. 3. Comparing the HF excitation energies for the singlet states to experiment, the  $^1E_g$  state is too low by 3468[cm<sup>-1</sup>] and the  $^1T_{2g}$  state by 3871[cm<sup>-1</sup>]. These errors are smaller than, but consistent with, the Cu<sup>+</sup>:NaF calculations. It also suggests that the results for Cu<sup>+</sup>:NaCl can also be brought into good agreement with the measured spectra by a nearly constant shift of all the levels together. The same is not true for the X-alpha calculations which give an error of 5161[cm<sup>-1</sup>] for the  $^1E_g$  state and 2339[cm<sup>-1</sup>] for the  $^1T_{2g}$  state. Also since these calculations do not directly determine the singlet and triplet states, they have reversed the order of the  $^1E_g$  and  $^3T_{2g}$  states. This would indicate that a great deal of caution must be exercised in using X-alpha results to interpret or predict the electronic spectra of impurities in crystals.

## V. Summary

The present calculations on the Cu<sup>+</sup> ion in alkali halide crystals are preliminary in nature, but very encouraging. The relative positions of the excited states as determined by theory and experiment are in excellent agreement. The neglect of electron correlation appears to be the only major reason for the disagreement with the absolute location of the peaks of the absorption bands measured by McCLURE[6] and PAYNE et al.[17],[21]. Our future work will focus on including this and the effects of spin-orbit interaction as well as the influence of the remainder of the lattice.

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